Journal of Organometallic Chemistry, 234 (1982) 299—308
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE CRYSTAL STRUCTURES OF 1-ALLYL-1-BROMO-3,4-BENZO-1-TELLURACYCLOPENTANE [$C_8H_8Te(C_3H_5)Br$], 1-PHENACYL-1-BROMO-3,4-BENZO-1-TELLURACYCLOPENTANE [$C_8H_8Te(C_8H_7O)Br$] AND 1-DEUTEROMETHYL-1-IODO-3,4-BENZO-1-TELLURACYCLOPENTANE [$C_8H_8Te(CD_3)I$]; THE *trans* EFFECT IN ORGANOTELLURIUM BROMIDES AND IODIDES *

RICHARD H. JONES and THOMAS A. HAMOR
Department of Chemistry, University of Birmingham, Birmingham B15 2TT (Great Britain)

(Received March 16th, 1982)

Summary

The crystal structures of the title compounds have been determined from three-dimensional X-ray counter data.

$C_8H_8Te(CH_2CH{=}CH_2)Br$ (I) is orthorhombic, space group *Pbca* with *a* 9.642(1), *b* 25.586(7), *c* 9.680(3) Å, $Z = 8$. The structure has been refined to R 5.2% for 1262 observed reflections.

$C_8H_8Te(CH_2COPh)Br$ (II) is orthorhombic, space group *Pccn* with *a* 23.593(6), *b* 14.337(3), *c* 9.180(2) Å, $Z = 8$. $R = 5.5\%$ for 1374 reflections.

$C_8H_8Te(CD_3)I$ (III) is orthorhombic, space group *Pbca* with *a* 11.200(3), *b* 15.976(2), *c* 23.328(3) Å, $Z = 16$. $R = 5.6\%$ for 2142 reflections.

In I and II, tellurium is coordinated in an approximately octahedral geometry by the organic residues and three halogen contacts, with Te—C and Te—Br distances in the ranges 2.14(1)—2.19(1) Å and 3.328(2)—3.368(2) Å in (I) and 2.12(1)—2.18(1) Å and 3.292(2)—3.391(2) Å in II.

In III, each of the two crystallographically independent complexes has tellurium coordinated in a distorted octahedral geometry. The Te—C bond lengths are 2.10(2)—2.16(2) Å. In each case two Te—I distances are in the range 3.596(2)—3.688(2) Å and a third, longer interaction (3.870(2) and 4.112(2) Å) completes the coordination.

In each of the structures I—III the three covalent Te—C bonds are oriented *cis* within the octahedra and exert a *trans* bond-lengthening effect on the Te—halogen interactions, precluding covalent-type bonding; the structures are essentially ionic, $(C_8H_8TeR)^+$ cations and halide anions forming extended arrays.

---

* Contribution from the Crystallography Unit, Universities of Aston and Birmingham.

0022-328X/82/0000—0000/$02.75

Introduction

Spectroscopic and conductivity studies [1] of a series of telluronium salts based on the 1-organo-3,4-benzo-1-telluracyclopentane cation $[C_8H_8TeR]^+$ show that in solvents of low polarity they are associated via weak ionic interactions. Association also occurs in the gas phase as indicated by mass spectrometric measurements. Although the detailed solid-state structures of a number of organotelluronium salts have been determined and association through relatively weak secondary bonding [2] is frequently found, that of only one 3,4-benzo-1-telluracyclopentane salt ($C_8H_8TeI_2$) has, as far as we are aware, been reported [3]. We now describe the crystal structures of the three compounds $C_8H_8Te(CH_2CH{=}CH_2)Br$ (I), $C_8H_8Te(CH_2COPh)Br$ (II) and $C_8H_8Te(CD_3)I$ (III), which have been determined in order to establish the coordination geometry of tellurium and the nature of the intermolecular interactions.

Experimental

Suitable crystals of compounds I—III were kindly supplied by Professor W.R. McWhinnie [1].

After preliminary examination by photographic methods, the final cell

TABLE 1

CRYSTAL AND EXPERIMENTAL PARAMETERS

	I	II	III
Molecular formula	$C_{11}H_{13}TeBr$	$C_{16}H_{15}OTeBr$	$C_9H_8D_3TeI$
Molecular weight	352.7	430.8	376.7
Crystal size (mm)	0.4 × 0.1 × 0.1	0.4 × 0.1 × 0.1	0.3 × 0.15 × 0.1
Cell constants (Å) a	9.642(1)	23.593(3)	11.200(3)
b	25.586(7)	14.337(1)	15.976(2)
c	9.680(3)	9.180(2)	23.328(3)
Cell volume (Å^3)	2388	3105	4174
Space group	*Pbca*	*Pccn*	*Pbca*
Z	8	8	16
Density (g cm^{-3})	1.962	1.843	2.398
Absorption coefficient (mm^{-1})	5.6	4.3	5.4
Data collection range (λ = 0.71069 Å) 2θ	4—50°	4—50°	4—50°
Scan range (ω°)	$1.35 + 0.35 \tan \theta$	$1.35 + 0.35 \tan \theta$	$1.10 + 0.35 \tan \theta$
Scan speed range (° min^{-1})	0.8—3.3	0.5—3.3	0.6—3.3
Total data measured	2104	2734	3660
Significant data [$I > 2.5\sigma(I)$]	1262	1374	2142
Least-squares weights $w = [\sigma^2(F) + KF^2]^{-1}$	$K = 0.0005$	$K = 0.004$	$K = 0.0016$
Final R (%)	5.22	5.46	5.63
Final R_w (%)	5.42	5.30	5.70

TABLE 2

FRACTIONAL ATOMIC COORDINATES FOR $[C_8H_8TeCH_2CH{=}CH_2]^+Br^-$ (I)

	x	y	z
Te	0.05974(9)	0.19619(4)	0.06082(9)
Br	0.2243(2)	0.2825(1)	−0.1375(2)
C(1)	0.2500(14)	0.1557(5)	0.0208(14)
C(2)	0.2276(13)	0.0998(5)	0.0584(15)
C(3)	0.3193(15)	0.0622(7)	0.0179(17)
C(4)	0.2975(19)	0.0106(8)	0.0501(21)
C(5)	0.1826(20)	−0.0040(6)	0.1199(21)
C(6)	0.0882(16)	0.0343(7)	0.1643(20)
C(7)	0.1083(14)	0.0858(6)	0.1306(17)
C(8)	0.0082(15)	0.1264(6)	0.1727(17)
C(9)	−0.0426(14)	0.1732(8)	−0.1311(16)
C(10′) [a]	0.0418(28)	0.1599(12)	−0.2530(28)
C(10″) [b]	0.0271(28)	0.1308(12)	−0.2124(26)
C(11′) [a]	0.0933(30)	0.1147(13)	−0.2910(33)
C(11″) [b]	0.0938(34)	0.1407(13)	−0.3283(32)

[a] Occupancy 0.54(5). [b] Occupancy 0.46(5).

dimensions and reflection intensities were measured with graphite-monochromated Mo-K_α radiation on an Enraf-Nonius CAD-4 diffractometer operating in the $\omega-2\theta$ scan mode. Two standard reflections were measured every hour to check the stability of the system. In the case of compound II some crystal decomposition occurred and appropriate scale factors were applied to compensate for a slight drop in intensity. Absorption corrections were not applied.

Structures I and II were solved by Patterson and Fourier methods and III by

TABLE 3

FRACTIONAL ATOMIC COORDINATES FOR $[C_8H_8TeCH_2COPh]^+Br^-$ (II)

	x	y	z
Te	0.18741(4)	0.14625(5)	0.23463(8)
Br	0.1829(1)	0.1356(1)	−0.1342(1)
C(1)	0.2025(6)	0.0028(8)	0.1978(12)
C(2)	0.1837(6)	−0.0501(9)	0.3370(15)
C(3)	0.1853(7)	−0.1452(10)	0.3436(19)
C(4)	0.1678(9)	−0.1903(12)	0.4639(20)
C(5)	0.1479(10)	−0.1392(12)	0.5864(20)
C(6)	0.1477(7)	−0.0453(11)	0.5784(15)
C(7)	0.1667(6)	0.0020(9)	0.4571(14)
C(8)	0.1706(6)	0.1086(9)	0.4605(14)
C(9)	0.0992(6)	0.1575(10)	0.1773(15)
C(10)	0.0610(6)	0.0896(10)	0.2564(15)
C(11)	0.0506(6)	−0.0035(10)	0.1966(14)
C(12)	0.0256(6)	−0.0722(13)	0.2810(17)
C(13)	0.0172(9)	−0.1626(14)	0.2271(24)
C(14)	0.0304(8)	−0.1850(12)	0.0892(22)
C(15)	0.0556(8)	−0.1168(11)	0.0050(19)
C(16)	0.0671(6)	−0.0275(12)	0.0564(16)
O	0.0385(5)	0.1133(8)	0.3714(11)

TABLE 4

FRACTIONAL ATOMIC COORDINATES FOR $[C_8H_8TeCD_3]^+I^-$ (III)

	x	y	z
Te(A)	—0.05567(10)	0.37119(6)	0.00774(5)
Te(B)	—0.40995(12)	0.45434(7)	—0.09314(5)
I(1)	—0.20465(12)	0.27675(7)	—0.11253(5)
I(2)	—0.25579(12)	0.56757(7)	0.02182(5)
C(1A)	0.0145(20)	0.3975(11)	0.0921(7)
C(2A)	—0.0637(17)	0.3522(9)	0.1330(7)
C(3A)	—0.0313(20)	0.3453(11)	0.1902(9)
C(4A)	—0.1079(26)	0.3044(12)	0.2285(9)
C(5A)	—0.2105(26)	0.2714(13)	0.2117(13)
C(6A)	—0.2450(20)	0.2790(12)	0.1538(9)
C(7A)	—0.1728(15)	0.3179(10)	0.1143(7)
C(8A)	—0.2078(16)	0.3254(11)	0.0537(7)
C(9A)	0.0244(17)	0.2515(11)	0.0018(8)
C(1B)	—0.2808(16)	0.4919(11)	—0.1541(7)
C(2B)	—0.3290(16)	0.4669(9)	—0.2119(8)
C(3B)	—0.2695(16)	0.4907(11)	—0.2622(9)
C(4B)	—0.3141(20)	0.4664(12)	—0.3148(9)
C(5B)	—0.4170(18)	0.4199(11)	—0.3194(8)
C(6B)	—0.4766(17)	0.3962(11)	—0.2682(8)
C(7B)	—0.4318(16)	0.4192(9)	—0.2163(7)
C(8B)	—0.4894(15)	0.3879(9)	—0.1610(7)
C(9B)	—0.5136(19)	0.5643(10)	—0.1067(9)

a combination of direct methods and Fourier syntheses. The refinements were by least squares, using anisotropic temperature factors for the non-hydrogen atoms. Hydrogen atoms were placed in calculated positions (C—H = 1.08 Å) "riding" on their respective carbon atoms. Refinement was terminated when all calculated shifts were $<0.1\sigma$. Details of crystal and experimental parameters are in Table 1. Final atomic coordinates for I—III are in Tables 2—4 *.

The allyl group of compound I exhibited disorder and two orientations of this group were refined with bond lengths and angles constrained to be close to expected values. Site occupation factors (constrained to add up to 1) were refined for the two orientations, and these converged to values of 0.54(5) and 0.46(5).

Computations were carried out largely on the CDC 7600 computer at the University of Manchester Regional Computer Centre with SHELX [4] and MULTAN 78 [5].

Results and discussion

Pertinent distances and angles are in Tables 5 (compounds I and II) and 6 (compound III). The tellurium coordination geometries in the three compounds are illustrated in Fig. 1—3.

---

[*] Lists of structure factors, thermal parameters and hydrogen atom coordinates are available from the authors.

TABLE 5

DISTANCES (Å) AND ANGLES (°) IN I AND II

Superscripts refer to the following equivalent positions:

Compound I: (i) $-\frac{1}{2}+x, \frac{1}{2}-y, -z$; (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$. Compound II: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $\frac{1}{2}-x, y, \frac{1}{2}+z$

	I	II		I	II
(a) Distances about Te			*(b) Angles about Te*		
Te—C(1)	2.142(14)	2.115(11)	C(1)—Te—C(8)	83.5(5)	86.6(5)
Te—C(8)	2.148(15)	2.179(12)	C(1)—Te—C(9)	95.9(5)	101.3(5)
Te—C(9)	2.185(15)	2.153(13)	C(8)—Te—C(9)	95.8(8)	94.3(5)
Te—Br	3.328(2)	3.391(2)	Br—Te—C(1)	79.0(3)	78.6(3)
Te—Br^{i}	3.363(2)	3.353(2)	Br—Te—C(8)	162.4(4)	158.9(4)
Te—Br^{ii}	3.368(2)	3.292(2)	Br—Te—C(9)	84.5(5)	74.3(4)
			Br—Te—Br^{i}	118.6(2)	113.5(2)
			Br—Te—Br^{ii}	99.7(2)	113.1(2)
			Br^{i}—Te—C(1)	160.4(4)	165.9(4)
			Br^{i}—Te—C(8)	78.5(4)	83.3(4)
			Br^{i}—Te—C(9)	78.3(5)	89.3(4)
			Br^{i}—Te—Br^{ii}	103.6(2)	86.6(2)
			Br^{ii}—Te—C(1)	80.3(3)	81.8(4)
			Br^{ii}—Te—C(8)	78.8(4)	79.0(4)
			Br^{ii}—Te—C(9)	173.7(5)	172.5(4)

(c) 3,4-Benzo-1-telluracyclopentane residue

Distances	I	II	Angles	I	II
C(1)—C(2)	1.49(2)	1.55(2)	Te—C(1)—C(2)	107(1)	107(1)
C(2)—C(3)	1.36(2)	1.37(2)	Te—C(8)—C(7)	107(1)	104(1)
C(3)—C(4)	1.37(2)	1.35(2)	C(1)—C(2)—C(3)	121(1)	121(1)
C(4)—C(5)	1.35(2)	1.42(3)	C(1)—C(2)—C(7)	119(1)	118(1)
C(5)—C(6)	1.41(2)	1.35(2)	C(3)—C(2)—C(7)	120(1)	121(1)
C(6)—C(7)	1.37(2)	1.38(2)	C(2)—C(3)—C(4)	121(1)	121(2)
C(2)—C(7)	1.39(2)	1.39(2)	C(3)—C(4)—C(5)	120(2)	120(2)
C(7)—C(8)	1.48(2)	1.53(2)	C(4)—C(5)—C(6)	120(2)	118(2)
			C(5)—C(6)—C(7)	120(2)	122(2)
			C(6)—C(7)—C(2)	119(1)	118(1)
			C(6)—C(7)—C(8)	121(1)	120(1)
			C(2)—C(7)—C(8)	120(1)	122(1)

(d) Allyl group (Compound I)

Distances		Angles	
C(9)—C(10′)	1.47(3)	Te—C(9)—C(10′)	120(1)
C(10′)—C(11′)	1.31(4)	C(9)—C(10′)—C(11′)	129(3)
C(9)—C(10″)	1.50(3)	Te—C(9)—C(10″)	116(1)
C(10″)—C(11″)	1.32(4)	C(9)—C(10″)—C(11″)	122(3)

(e) Phenacyl group (Compound II)

Distances		Angles	
C(9)—C(10)	1.51(2)	Te—C(9)—C(10)	114(1)
C(10)—C(11)	1.46(2)	C(9)—C(10)—O	119(1)
C(10—O	1.23(2)	C(9)—C(10)—C(11)	121(1)
C(11)—C(12)	1.39(2)	O—C(10)—C(11)	120(1)
C(12)—C(13)	1.40(3)	C(10)—C(11)—C(12)	121(1)
C(13)—C(14)	1.34(3)	C(10)—C(11)—C(16)	122(1)
C(14)—C(15)	1.38(2)	C(11)—C(12)—C(13)	121(2)
C(15)—C(16)	1.39(2)	C(12)—C(13)—C(14)	121(2)
C(16)—C(11)	1.39(2)	C(13)—C(14)—C(15)	117(2)
		C(14)—C(15)—C(16)	123(2)
		C(15)—C(16)—C(11)	119(2)
		C(16)—C(11)—C(12)	118(2)

TABLE 6

DISTANCES (Å) AND ANGLES (°) IN III

Superscripts refer to the following equivalent positions: (i) $-x$, $1-y$, $-z$; (ii) $-1-x$, $1-y$, $-z$

(a) Distances about Te

Te(A)—C(1A)	2.160(17)	Te(B)—C(1B)	2.115(16)
Te(A)—C(8A)	2.141(17)	Te(B)—C(8B)	2.104(16)
Te(A)—C(9A)	2.117(16)	Te(B)—C(9B)	2.130(18)
Te(A)—I(2^{i})	3.688(2)	Te(B)—I(2)	3.667(2)
Te(A)—I(1)	3.596(2)	Te(B)—I(2^{ii})	4.112(2)
Te(A)—I(2)	3.870(2)	Te(B)—I(1)	3.680(2)

(b) Angles about Te

C(1A)—Te(A)—C(8A)	84.3(7)	C(1B)—Te(B)—C(8B)	85.8(7)
C(1A)—Te(A)—C(9A)	94.7(7)	C(1B)—Te(B)—C(9B)	92.2(7)
C(8A)—Te(A)—C(9A)	93.5(7)	C(8B)—Te(B)—C(9B)	94.2(7)
I(2^{i})—Te(A)—C(1A)	77.0(5)	I(2)—Te(B)—C(1B)	91.7(5)
I(2^{i})—Te(A)—C(8A)	159.5(5)	I(2)—Te(B)—C(8B)	176.9(5)
I(2^{i})—Te(A)—C(9A)	80.0(6)	I(2)—Te(B)—C(9B)	87.6(5)
I(2^{i})—Te(A)—I(1)	113.8(1)	I(2)—Te(B)—I(2^{ii})	100.1(1)
I(2^{i})—Te(A)—I(2)	110.4(1)	I(2)—Te(B)—I(1)	100.1(1)
I(1)—Te(A)—C(1A)	164.0(5)	I(2^{ii})—Te(B)—C(1B)	156.7(5)
I(1)—Te(A)—C(8A)	83.0(4)	I(2^{ii})—Te(B)—C(8B)	82.9(5)
I(1)—Te(A)—C(9A)	76.5(5)	I(2^{ii})—Te(B)—C(9B)	68.5(6)
I(1)—Te(A)—I(2)	97.9(1)	I(2^{ii})—Te(B)—I(1)	123.6(1)
I(2)—Te(A)—C(1A)	88.6(5)	I(1)—Te(B)—C(1B)	73.1(5)
I(2)—Te(A)—C(8A)	76.9(5)	I(1)—Te(B)—C(8B)	77.4(5)
I(2)—Te(A)—C(9A)	169.6(6)	I(1)—Te(B)—C(9B)	163.4(5)

(c) 3,4-Benzo-1-telluracyclopentane residue

Distances	Residue A	Residue B	Angles	Residue A	Residue B
C(1)—C(2)	1.48(2)	1.51(2)	Te—C(1)—C(2)	106(1)	106(1)
C(2)—C(3)	1.39(3)	1.40(3)	Te—C(8)—C(7)	107(1)	107(1)
C(3)—C(4)	1.40(3)	1.38(3)	C(1)—C(2)—C(3)	120(2)	121(2)
C(4)—C(5)	1.32(3)	1.38(3)	C(1)—C(2)—C(7)	120(2)	121(2)
C(5)—C(6)	1.41(3)	1.42(3)	C(3)—C(2)—C(7)	120(2)	119(2)
C(6)—C(7)	1.37(2)	1.36(2)	C(2)—C(3)—C(4)	119(2)	120(2)
C(2)—C(7)	1.41(3)	1.38(2)	C(3)—C(4)—C(5)	122(2)	122(2)
C(7)—C(8)	1.47(2)	1.53(2)	C(4)—C(5)—C(6)	119(2)	118(2)
			C(5)—C(6)—C(7)	121(2)	120(2)
			C(6)—C(7)—C(2)	119(2)	122(2)
			C(6)—C(7)—C(8)	122(2)	121(2)
			C(2)—C(7)—C(8)	120(2)	118(2)

There are no discrete C_8H_8TeRBr or C_8H_8TeRI molecules and the structures can be considered to consist of $(C_8H_8TeR)^+$ cations and halide anions. In each case the coordination about tellurium is approximately octahedral with the 1-organo group in the axial position normal to the 3,4-benzo-1-telluracyclopentane (C_8H_8Te) ring system and halogen ions in the remaining three sites *trans* to the Te—C bonds. These link neighbouring cations into extended arrays.

The bromide salts I and II have similar structures (see Table 5). The coordination octahedra are, however, considerably distorted. Angular deviations from ideal values of up to 28.6 and 23.5° occur in I and II, respectively. Te—C bond lengths range from 2.115(11) to 2.185(15) Å with mean values 2.158 and

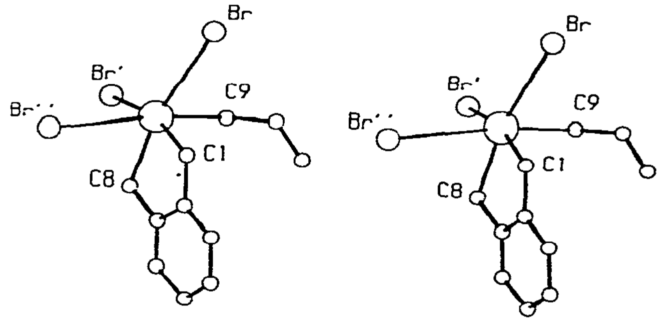

Fig. 1. The tellurium coordination in I. The prime and double prime refer to the equivalent positions specified in Table 5 as (i) and (ii).

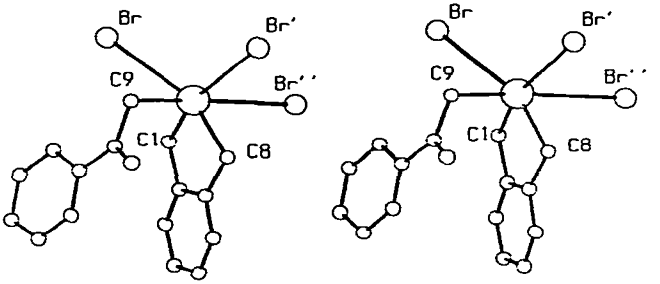

Fig. 2. The tellurium coordination in II. Primes have the same meaning as for Fig. 1.

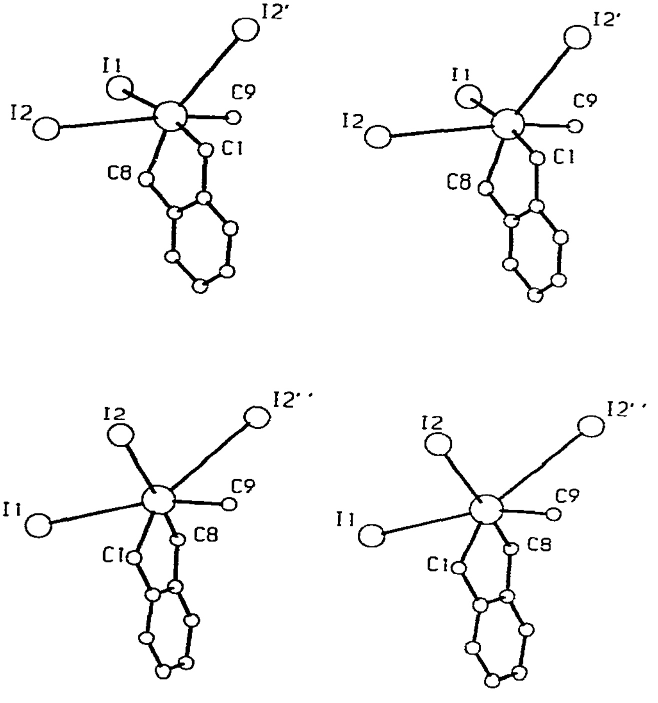

Fig. 3. The tellurium coordination in III; upper diagram Te(A), lower diagram Te(B). Prime and double prime refer to the equivalent positions specified in Table 6 as (i) and (ii).

2.149 Å in I and II. These distances are in good agreement with the Te—C distances in $C_8H_8TeI_2$ [3], 2.145(12) and 2.139(12) Å and with the sum of the single bond covalent radii, 2.14 Å [6]. The Te—Br distances 3.292(2)—3.391(2) Å, mean 3.353 Å (I) and 3.345 Å (II) are intermediate between the Van der Waals and covalent sum of radii, 4.15 and 2.51 Å [6]. The near equality of the Te—Br distances contrasts with the situation in the crystal structures of diphenyltellurium dibromide [7], 1-thia-4-telluracyclohexane-4,4-dibromide [8] and (4-ethoxyphenyl)tellurium tribromide [9] in which Te—Br distances ranging from the standard [6] covalent to the Van der Waals distance occur. Similar Te—Br bond lengths are also found in the tellurium(II) complexes bromo(thiourea)phenyltellurium [10], and the corresponding ethylenethiourea [11] and ethyleneselenourea [12] compounds. There is, however, some tendency for the Te—Br interactions to cluster in two ranges, 2.5—3.1 Å and 3.6—3.9 Å; those within the former range are generally classified as at least partially covalent.

The Te—Br lengths in our compounds I and II do not fall into either of these ranges. The bonding appears to be similar in nature to the Te—halogen bonding in triphenyltelluronium chloride [13] where the Te—Cl lengths, mean 3.20(2) Å, are also almost exactly half-way between the Pauling [6], Van der Waals and covalent distances.

In the iodide III, tellurium has a somewhat different coordination geometry. In each of the two crystallographically independent $[C_8H_8Te(CD_3)]^+$ cations (A and B), tellurium is coordinated approximately octahedrally. The Te—C bond lengths 2.104(16)—2.160(17) Å, mean 2.128 Å are in good agreement with the corresponding lengths in I and II and with the sum of the covalent radii of Te and C. However, in each case one of the Te—I distances is significantly longer than the other two. Thus four of the Te—I distances are in the range 3.596(2)—3.688(2) Å, mean 3.658 Å and the other two are 3.870(2) Å (Te(A)) and 4.112(2) Å (Te(B)) (see Table 6). These values are intermediate between the sums of the Van der Waals and covalent radii, 4.35 and 2.70 Å, respectively [6], but even the shorter Te—I distances are somewhat closer to the Van der Waals distance than to the covalent. Of the two independent iodide ions, I(1) is involved in only two of the shorter bonds, whereas I(2) is involved in two short and also the two long Te—I interactions. Maximum angular deviations from an ideal octahedral geometry about Te are 23.8° (A) and 33.6° (B). It is noteworthy that the major angular deviations in the Te(B) octahedron involve the weakly linked $I(2^{ii})$.

Approximately octahedral coordination of tellurium with Te—I lengths falling into two categories, 2.95 ± 0.2 Å and 3.8 ± 0.2 Å occurs [3,9,14—19] in a number of organotellurium iodides. The shorter bonds, although generally longer than the sum of the covalent radii, have been considered as essentially covalent. The longer interactions have been classified as intermolecular or secondary [2] bonds. Thus in $Me_2TeI_2 \cdot I_2$ [14] there are two short Te—I distances of 2.809(2) and 3.082(2) Å and two long ones of 3.938(2) and 3.957(2) Å, and in β-Me_2TeI_2 [15] which consists of Me_3Te^+ and $MeTeI_4^-$ ions, the cationic Te has three iodide ions at distances in the range 3.84(1)—4.00(1) Å, while the anionic Te is involved in five interactions with iodine, four in the range 2.84(1)—2.98(1) Å and the fifth, 3.88(1) Å. In $C_8H_8TeI_2$ [3] there are two short Te—I bonds, 2.900(1) and 2.928(1) Å, and two long ones, 3.653(1) and 3.878(1) Å.

Vikane [11] has noted with reference to organotellurium(II) bromide complexes that only long, weak interactions are found *trans* to Te—C bonds. A similar effect has been noted in the structure of 2,6-diacetylpyridinetellurium(IV) trichloride [20]. The *trans* bond-lengthening effect of covalently-bound carbon manifests itself also in organotellurium(IV) bromides and iodides [3,7—9,14—19] and affords a partial rationalisation for the observed variation in Te—halogen contact distances; here short Te—halogen bonds are *trans* to each other, but are never *trans* to a Te—C bond. In our compounds I—III the arrangement of the organic ligands is such that the remaining vertices of the coordination octahedra are all *trans* to covalently-bound carbon; the Te—halogen interactions are all weak and the bonding may be classified as secondary and is probably largely ionic in nature.

That the Te—Br coordination distances in I and II are intermediate between the two characteristic ranges previously found [7—12] may be rationalised on the basis of the observation that if a bromine is involved in a covalent type interaction with tellurium, any interactions with other tellurium atoms, which are *trans* to a Te—C bond, will be weak and involve long secondary bonds. In the previously examined [7—12] compounds each bromine involved in a secondary Te—Br bond is also involved in a covalent Te—Br bond, and the secondary interactions can be classified as long. In compounds I and II, however, there are no covalent Te—Br bonds, the bromide ions are shared equally between neighbouring tellurium atoms and the secondary bonds are relatively short and strong.

The 3,4-benzo-1-telluracyclopentane ring systems in compounds I—III are not planar. The carbon atoms of the C_8H_8 residues are approximately co-planar (to within ±0.02 Å (I), ±0.07 Å (II), ±0.02 Å (III) (residue A) and ±0.05 Å (III) (residue B)), but the tellurium atoms are displaced from their respective mean planes by 0.46 Å in I, 0.27 Å in II, 0.38 Å in III (Te(A)) and 0.30 Å (Te(B)). In every case the displacement is towards C(9). The C_8H_8Te ring of the diiodide, $C_8H_8TeI_2$, is, however, planar to within 0.04 Å with the tellurium atom only 0.03 Å from the plane [3]. Presumably the much larger displacement of the tellurium atom in compounds I—III is related to the unsymmetrical nature of the bonding normal to the C_8H_8Te plane.

Bond lengths and angles within the organic ligands are unexceptional.

In all three compounds the complex cations are associated via the halide anions, but the nature of the association differs. In I bromide ions and organotellurium cations form infinite layers perpendicular to the crystallographic *y* axis at $y = \frac{1}{4}$ and $\frac{3}{4}$. In II, cations and anions form infinite cross-linked double chains parallel to *z*. In III, if only the four shorter Te—I bonds are considered, the cations are associated into discrete centrosymmetric tetramers involving eight-membered rings $\overline{\text{Te(A)—I(1)—Te(B)—I(2)—Te(A}^{i}\text{)—I(1}^{i}\text{)—Te(B}^{i}\text{)—I(2}^{i}\text{)}}$. The Te(A)—I(2) interaction of 3.870(2) Å is within the tetramer, but the very long Te(B)—I(2^{ii}) interaction of 4.112(2) Å links the tetramers into chains parallel to *x*.

There are no abnormally short Te···Te or halide···halide contacts. The closest approach of two tellurium atoms is 4.192(2) Å in II and of two bromide ions, 4.558(3) Å, also in II. The next shortest Te···Te contact is 4.316(2) Å in compound III. The shortest I···I distance is 4.603(3) Å. The Te···Te distances are slightly smaller than the sum of the Pauling Van der Waals radii (4.4 Å) but are greater than the radius sum if the value 2.06 suggested by Bondi [21] is used for the radius of tellurium. The inter-halogen distances are all substantially greater than the Van der Waals distance.

Acknowledgements

We thank Professor W.R. McWhinnie and co-workers for suggesting this problem and materials, and the University of Birmingham for the award of a Research Studentship to R.H.J.

References

1 A.Z. Al-Rubaie, W.R. McWhinnie, P. Granger and S. Chapelle, J. Organometal. Chem., 234 (1982) 287.
2 N.W. Alcock, Advan. Inorg. Chem. Radiochem., 15 (1972) 1.
3 C. Knobler and R.F. Ziolo, J. Organometal. Chem., 178 (1979) 423.
4 G.M. Sheldrick, SHELX, Program for Crystal Structure Determination, University of Cambridge, 1978.
5 P. Main, S.E. Hull, L. Lessinger, G. Germain, J.P. Declercq and M.M. Woolfson, MULTAN 78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, Universities of York and Louvain, 1978.
6 L. Pauling, The Nature of the Chemical Bond, 3rd Ed., Cornell University Press, Ithaca, New York, 1960.
7 G.D. Christofferson and J.D. McCullough, Acta Crystallogr., 11 (1958) 249.
8 C. Knobler and J.D. McCullough, Inorg. Chem., 11 (1972) 3026.
9 P.H. Bird, V. Kumar and B.C. Pant, Inorg. Chem., 19 (1980) 2487.
10 O. Foss and S. Husebye, Acta Chem. Scand., 20 (1966) 132.
11 O. Vikane, Acta Chem. Scand., A, 29 (1975) 738.
12 O. Vikane, Acta Chem. Scand., A, 29 (1975) 763.
13 R.F. Ziolo and M. Extine, Inorg. Chem., 19 (1980) 2964.
14 H. Pritzkow, Inorg. Chem., 18 (1979) 311.
15 F. Einstein, J. Trotter and C. Williston, J. Chem. Soc. A, (1967) 2018.
16 H. Hope, C. Knobler and J.D. McCullough, Inorg. Chem., 12 (1973) 2665.
17 J.D. McCullough, Inorg. Chem., 12 (1973) 2669.
18 J.D. McCullough, Inorg. Chem., 14 (1975) 1142.
19 L.Y.Y. Chan and F.W.B. Einstein, J. Chem. Soc. Dalton, (1972) 316.
20 H.J. Gysling, H.R. Luss and S.A. Gardner, J. Organometal. Chem., 184 (1980) 417.
21 A. Bondi, J. Phys. Chem., 68 (1964) 441.